Origin of Pyrite Concretions from the Dunkirk Shale Member of the Canadaway Formation (Devonian), Western New York

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By

Zhe Yang
The Ohio State University
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Approved by

Loren E. Babcock
School of Earth Sciences

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ABSTRACT

SEM and EDX technology has been used to analyze pyrite concretions from black shale layers of the Dunkirk Shale Member of the Canadaway Formation (Upper Devonian) at Point Gratiot, Dunkirk, New York. Point Gratiot is the type locality of the Dunkirk Shale Member. Black-colored spores observed in studied samples are identified as *Protosalvinia*. Two sizes ranges of spores are present. Smaller spores range in size from 0.5 to1 mm in diameter. Larger spore capsules are 4 to 6 mm in diameter. Small spores tend to be dispersed across bedding planes. Pyrite framboids were observed on the surface of larger spores. These larger spores may in fact be spore capsules. Framboidal pyrite, presumed to have developed around bacteria, are associated with the larger spores. Most pyrite concretions in the studied samples are surrounded by halos of limonite and anhydrous iron sulfide, presumably the result of of weathering.

Acknowledgments

I would like to thank Professor Loren E. Babcock for his guidance, and support of this senior thesis. He is wise and humorous. It is my honor to have Professor Loren E. Babcock as my thesis advisor and my mentor in the geology field. It is a special experience for me to work with him. This thesis would not have been accomplished without his help and encouragement.

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INTRODUCTION

Pyrite is one of the most common sedimentary minerals. Pyrite in the form of concretions has been shown to precipitate in association with organic material within microbial halos surrounding decaying material (Borkow and Babcock, 2003). Pyrite concretions of sedimentary origin usually form in black or dark grey shales (Babcock and Speyer, 1987).

The objective of this research was to explore the origins of the pyrite concretions from a prominent pyrite-bearing layer of black shale in the Dunkirk Shale Member of the Canadaway Formation (Upper Devonian) along the Lake Erie shore at Point Gratiot, Dunkirk, New York. This locality has one of the best exposed pyrite concretion layers known anywhere in the world (see Tesmer, 1967; Borkow and Babcock, 2003; Goldberg, 2006 for some additional examples). The outcrop of black shale at the Lake Erie beach is about 5 m thick, but the most prominent pyrite bed is confined to a single horizon. Pyrite concretions are in the lower part of the outcrop, and the size of most pyrite concretions is up to a few cm in diameter. Pyrite concretions usually start within a microbial halo and extend to the limits of the microbial biofilm surrounding the decaying organism (Borkow and Babcock, 2003). Pyrite concretions are usually caused by the preservation of biomineralized microfossils (fungi and/or bacteria). SEM (Scanning Electron Microscope) analysis and EDX (Energy Dispersive X-ray Spectroscopy) allow us to better understand organic matter, organic structures, and the chemical composition of pyrite concretion, providing information about the origin of pyrite. We can interpret the processes of concretion formation by analyzing their geological and biological origins. Besides, we can also develop a deeper comprehension about how depositional environment and geological history affects the concretions during the sedimentational process.

Using SEM (Scanning Electron Microscope) and EDX (Dispersive X-ray Spectroscopy) analysis we can figure out the chemical composition and the detailed organic structure of the studied concretions. Large euhedral crystals, and pyrite framboids have been observed in the specimens. Framboids indicates the presence of an anoxic environment during the time of deposition. It seems that concretions nucleate around decaying organisms due to action of microbial biodegraders (Borkow and Babcock, 2003). Large numbers of pyrite concretions occur in the Dunkirk Shale. Work reported here shows that the concretions contain fossilized spores. Organic decay of the spores appears to have played a significant role in the precipitation of pyrite. Organic matter was observed to be associated with pyrite framboids inside the spores under the stereomicroscope and under the SEM. Spores are of two sizes, large and small, and both are identified as *Protosalvini*a.

GEOLOGIC SETTING

General Geology

The Dunkirk Shale Member of the Canadaway Formation is an organic-rich, black shale (Tesmer, 1967). It contains numerous miospores (Richardson and Ahmed, 1988).The Dunkirk Shale is the stratigraphic equivalent of the Huron Shale Member of the Ohio Shale (Hellstrom and Babcock, 2000). Its crops out and is well exposed along the Lake Erie shore especially at Point Gratiot, Dunkirk, Chautauqua County, New York. The Dunkirk Shale Member is one regionally recognized unit that is part of an Upper Devonian black shale succession that is broadly expressed across the Appalachian Basin. The thickness of the Dunkirk Shale Member ranges from 335 to 426 m (David, Lombardi and Martin, 2004).

The Canadaway Formation is part of the Arkwright Group (Upper Devonian), which contains strata from the top of the Ellicott Shale Member of the Chadakoin Formation through the Canadaway Formation. The Arkwright Group includes gray and black shales, plus abundant interbedded gray siltstones, approximately 460 m thick (Tesmer, 1967).

The Dunkirk Shale Member is the lowest member of the Canadaway Formation. It is a platy black shale unit that contains pyrite nodules and limestones concretions (sometimes septarian concretions) ranging in size from 0.3-1.5 m in diameter. Equivalent black shales containing large calcareous concretions and small pyrite concretions extend from southwestern New York through western Pennsylvania, Ohio, northernmost West Virginia, Kentucky, and Tennessee, and is known by various local names (Huron Member of the Ohio Shale, Chattanooga Shale). The rest of the six members of the Canadaway Formation are the Northeast, Shumla, Westfield, Laona, Gowanda, and South Wales members. The Laona and Shumla Members mostly consist of light gray siltstone. The Northeast Member is largely composed of gray calcareous shale and interbedded siltstones.The Gowanda Member contains gray to black shale. The Westfield and South Wales Members contain mostly black shales.

Figure 1. Photo of the lower part of the outcrop at Point Gratiot, Dunkirk, New York, showing limonite staining around pyrite.

Depositional environment

The Dunkirk Member contains various microfossils. Macrofossils include various brachiopods and occasional driftwood fragments. The Dunkirk lacks much macroscopic trace fossil evidence. The Dunkirk Shale, located in the Appalachian Basin, was deposited during the Late Devonian (Tesmer, 1967). Organic-rich shale of this type usually results from deposition in one of four kinds of environment: 1, marine environment; 2, non-marine environment; 3, continental environment; or 4, marine-continental transitional environment. The Dunkirk Shale was deposited in a marine basin in an epeiric sea but probably relatively close to the marine-continental transitional environment. A sudden change in sea level, due to basin downdropping, may have been responsible for the rapid shift from from shallow deposits to black shales of the Dunkirk Shale. The formation of the pyrite concretions of Dunkirk Member requires anoxic conditions for the pyrite crystals to form. This anoxia may formed in the sediment, but also perhaps in the water column (Hellstrom and Babcock, 2000). The black shales suggest diminished siliciclastice sediment influx into an area of limited oxygen.

Lester (2017), recently studied the origin of pyrite concretions in the Huron Member of the Ohio Shale in central Ohio. She found two sizes of *Protosalvinia*, and the larger ones were associated with the formation of pyrite concretions, just like here in the Dunkirk Shale. The pyrite beds may represent the same sedimentologic event, but are distantly separated in different parts of the Appalachian Basin. Perhaps a large tropical storm or hurricane dispersed *Protosalvinia* spores widely across the basin.

Figure 2. Close-up view of the pyrite concretion bed in the outcrop. Red arrow indicates the level of pyrite concretion bed.

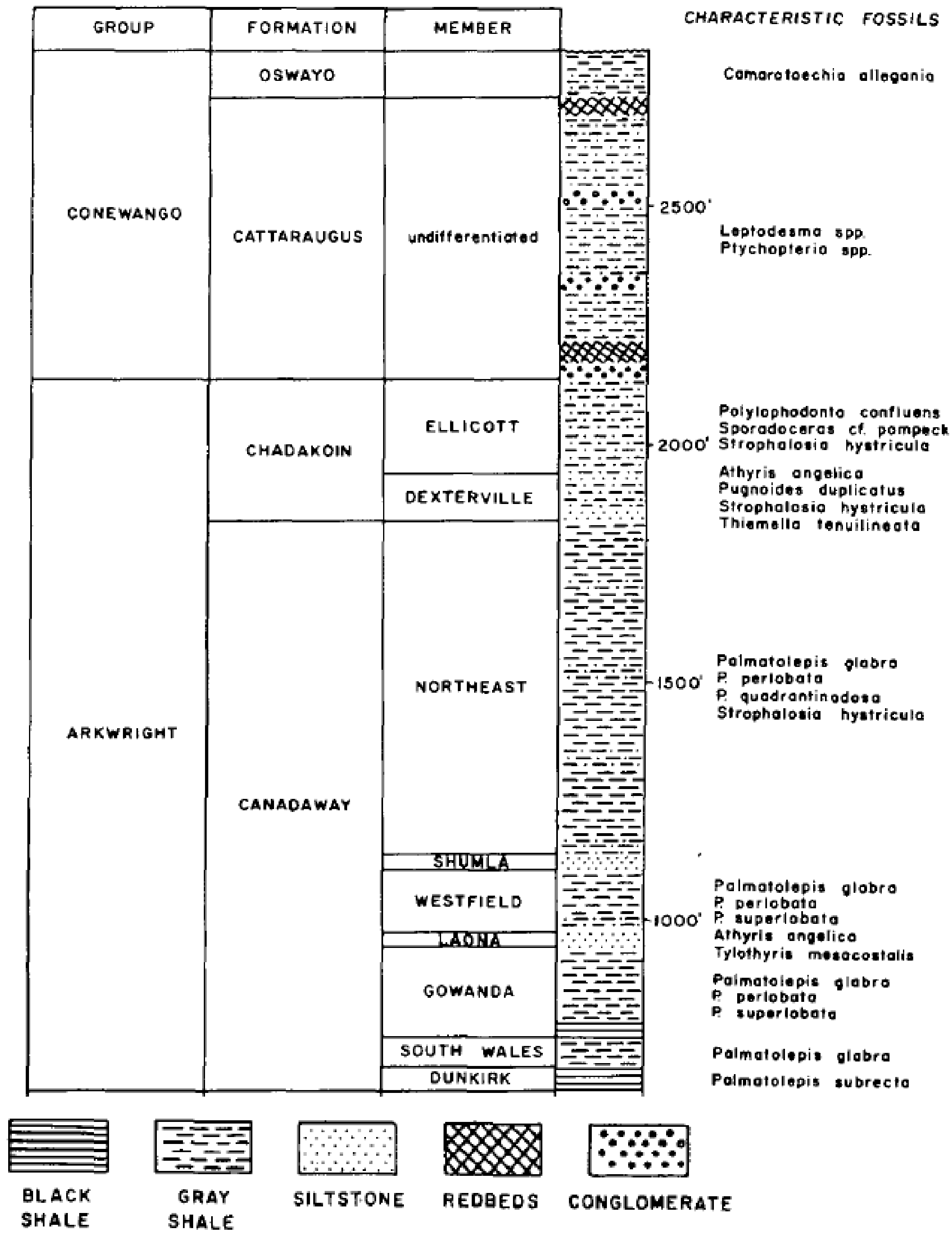

Figure 3. Stratigraphic column for Devonian strata of southwestern New York State (from Tesmer, 1967).

METHOD

Collecting samples

Studied rock samples were collected form Point Gratiot, Dunkirk, New York (Figure 2), where the Dunkirk Shale Member of the Canadaway Formation (Upper Devonian) is exposed. Three individual rock samples were collected. Most show pancake-shaped concretions of pyrite, or iron sulfide, FeS_2.

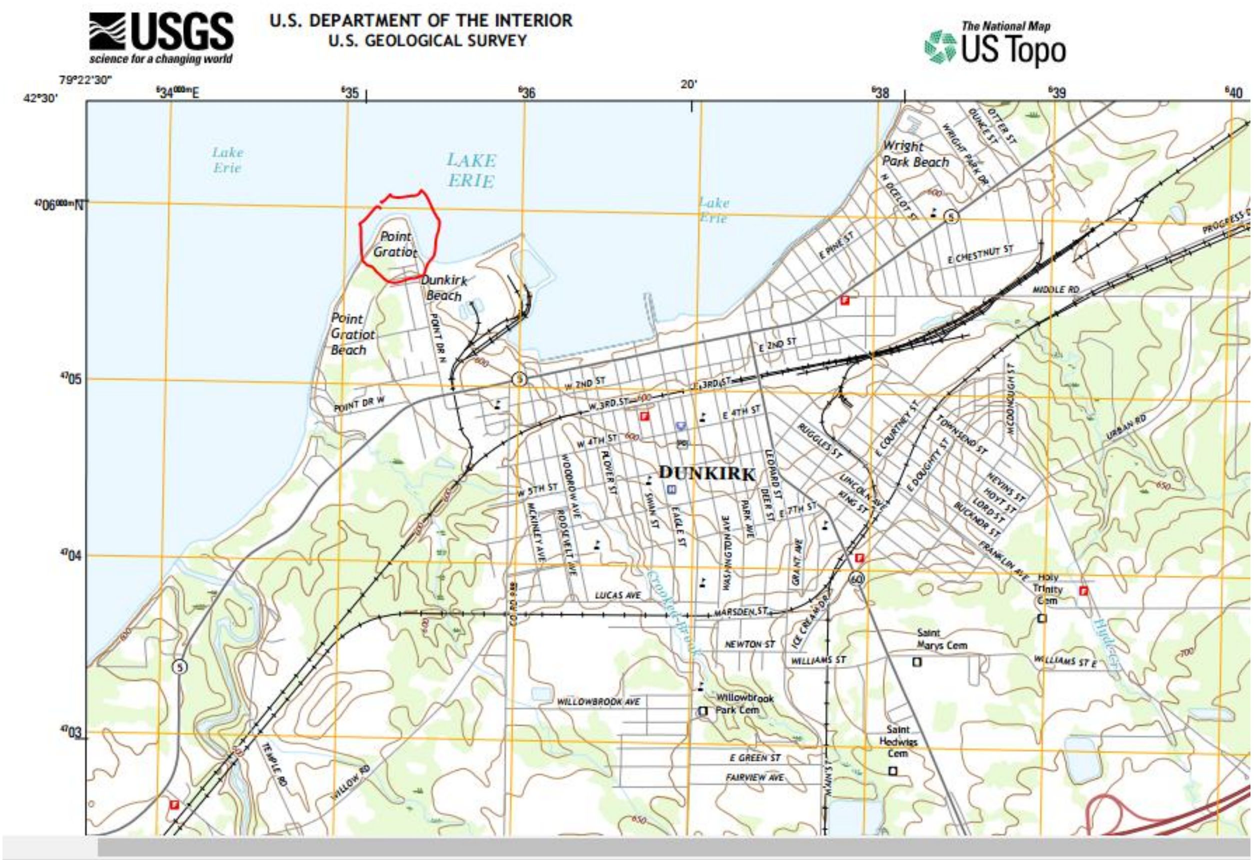

Figure 4. Location of sampled outcrop of the Dunkirk Shale Member of the Canadaway Formation at Point Gratiot, Dunkirk, Chautauqua County, New York. Red circle indicates the position where the samples were collected. (U.S. Geological Survey, 2016; Dunkirk, New York 7.5 minute Quadrangle, scale 1:24000.)

Sample analysis microscopy

In general, the shape of crystals is crucial for determing the origin of pyrite concretions. Organic matter and morphology of pyrite concretion were studied by using the SEM (Scanning Electron Microscope) in the School of Earth Science at The Ohio State University. The major portion of SEM are electron optical column, electronics and a vacuum system. Samples were put into the sample holder and held with a copper conductive tape in order to control charging. An electron gun generated an electron beam that was concentrated on a fine spot with a size of 4 micrometers on the sample surface. The accelerating voltages of SEM varied from 100 to 30000V. The beam was scanned in a rectangular raster over the surface of samples to generate several images and displays in the computer screen; these yielded information about crystal orientation, crystalline structure and external morphology.

Sample analysis spectroscopy

The chemical composition of pyrite concretions can be interpreted by using the Energy Dispersive X-ray Spectroscopy (EDX). EDX is a useful X-ray analytical method to identify the elemental composition of specimen. The Energy Dispersive detector can detect X-rays and transmits the signal as a graph or spectrum of intensity versus X-ray energy. The graph indicates peaks corresponding to the chemical elements and the composition of the analyzed sample.

RESULTS

Three slabs of black shale, all from the same layer in the lower part of the Dunkirk Shale Member of the Canadaway Formation (Devonian: Famennian) from Point Gratiot, Dunkirk, Chautauqua County, New York were studied. The slabs are float blocks, but easily tied into the stratigraphy at the outcrop. The pyrite layer crops out over a great distance near water level.

Each of the studied slabs contained pyrite concretions, approximately 2 to 18 mm in diameter and 2 to 3 mm thick. Some pyrite concretions are compound, and therefore larger, up to 50 mm in maximum dimension. Most pyrite concretions are surrounded by halos of limonite or another anhydrous iron sulfide, presumably the result of weathering. Inside some of the pyrite concretions, framboids are evident. Other mineral matter, including probably clay minerals, also appears to be present in some.

Also present on the studied slabs are black-colored spores identified as *Protosalvinia.* Two size ranges of spores are present. Smaller spores range in size from 0.5 to1 mm in diameter, and they are compressed. Larger spores (or spore capsules) are 4 to 6 mm in diameter.

When viewed under a stereomicroscope, small spores are scattered over the samples, on the same bedding plane as the pyrite concretions. All are compressed, and appear to be preserved as carbonized specimens. Some are rounded, whereas others seem more angular. Commonly small spores are clustered close together. Larger spores are also present on the black shale slabs. Most are encrusted by pyrite, and some appear to be the nuclei for pyrite concretions.

Figure 5. Pyrite concretions on bedding plane from the lower Dunkirk Shale Member of the Canadaway Formation (Devonian), Point Gratiot, Dunkirk, New York, showing general

morphology and limonite halos due to weathering. Also present are small black spores (red circle). Bar scale in mm.

Figure 6. Close-up view of specimen in Figure 2 showing pyrite concretions and small black spores on bedding plane from the lower Dunkirk Shale Member of the Canadaway Formation (Devonian), Point Gratiot, Dunkirk, New York. Bar scale in mm.

Figure 7. Pyrite concretions and small black spores on bedding plane from the lower Dunkirk Shale Member of the Canadaway Formation (Devonian), Point Gratiot, and Dunkirk, New York. Bar scale in mm.

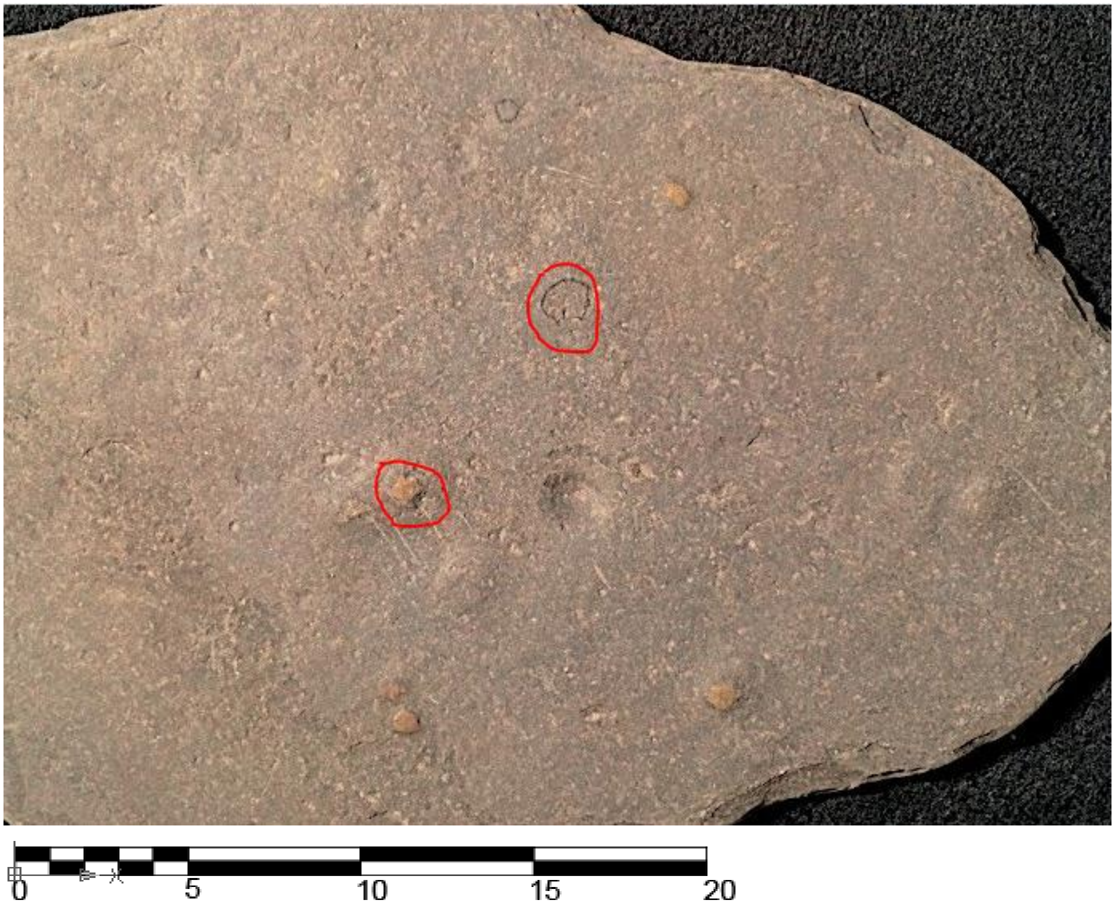

Figure 8. Pyrite concretions, small black spores, and large spore surrounded by pyrite concretion (red circle) on bedding plane from the lower Dunkirk Shale Member of the Canadaway Formation (Devonian), Point Gratiot, and Dunkirk, New York. Bar scale in mm.

Figure 9. SEM photomicrograph showing small spores (black) on bedding plane.

Figure 10. SEM photomicrograph showing pyrite concretion associated with organic matter.

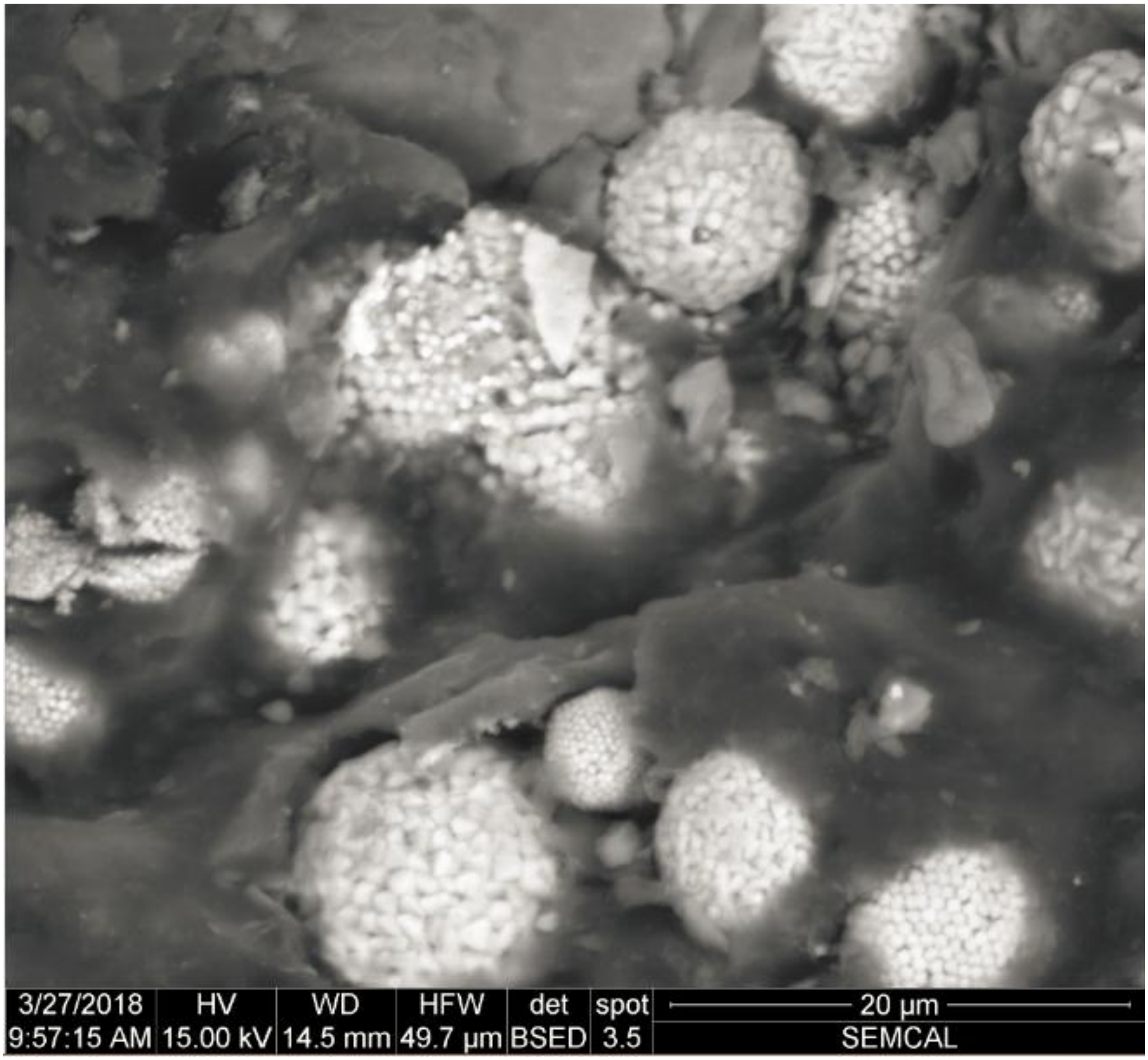

Figure 11. Close-up SEM photomicrograph showing view of a pyrite framboid on the surface of pyrite concretion.

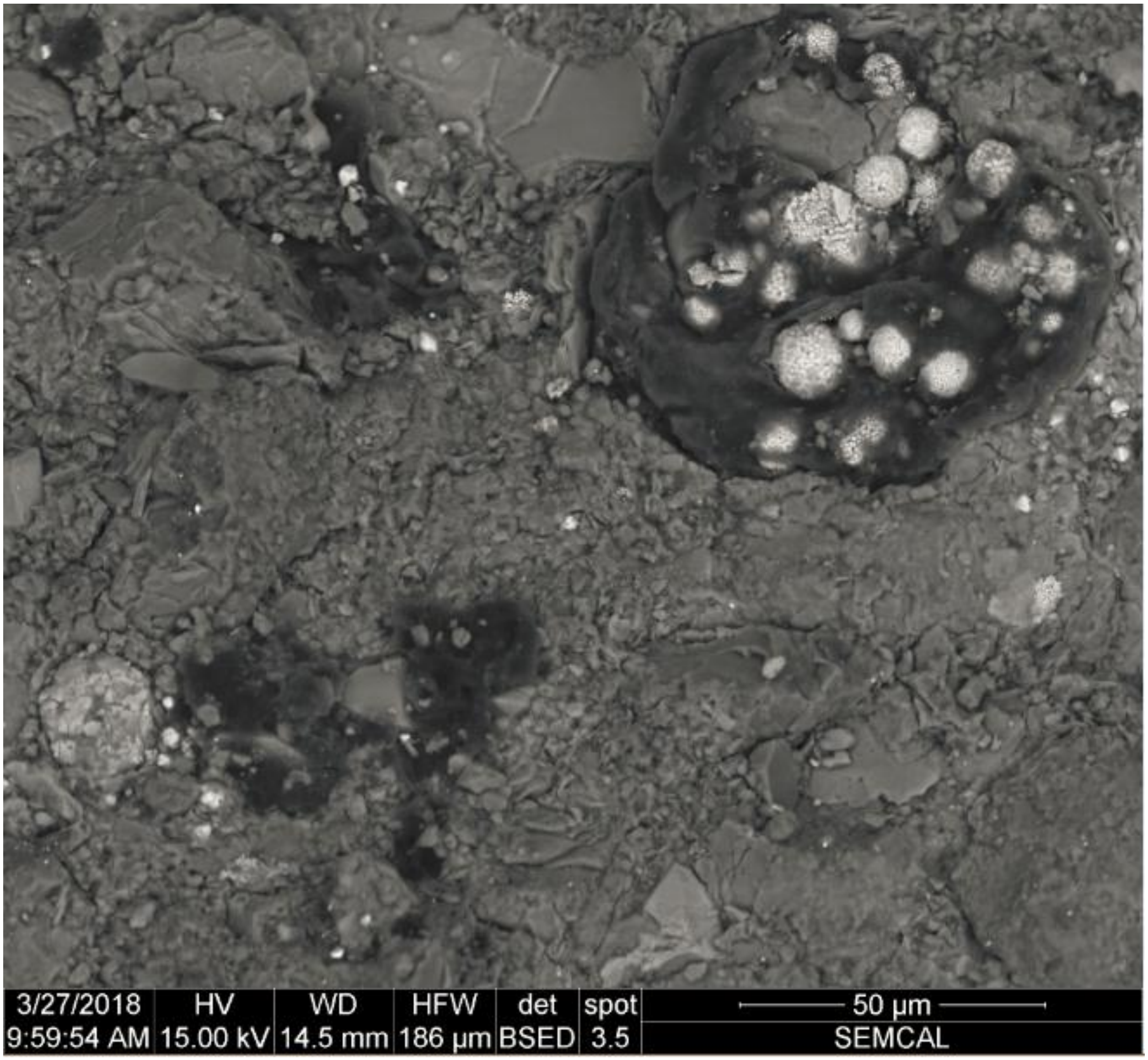

Figure 12. SEM photomicrograph showing the relationship of a pyrite concretion to nearby organic matter (black).

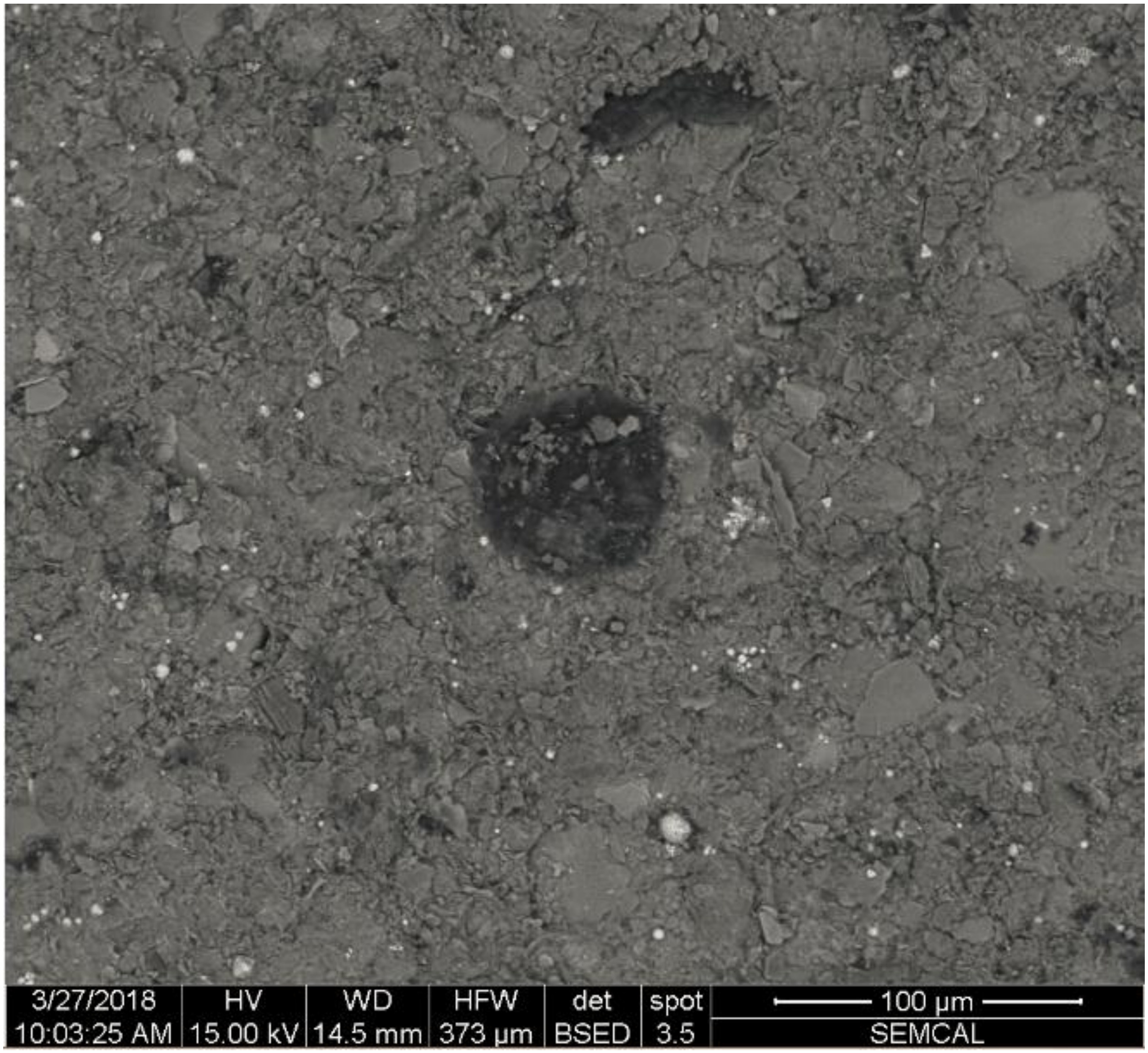

Figure 13. SEM photomicrograph showing black spore, *Protosalvinia*, on a bedding plane.

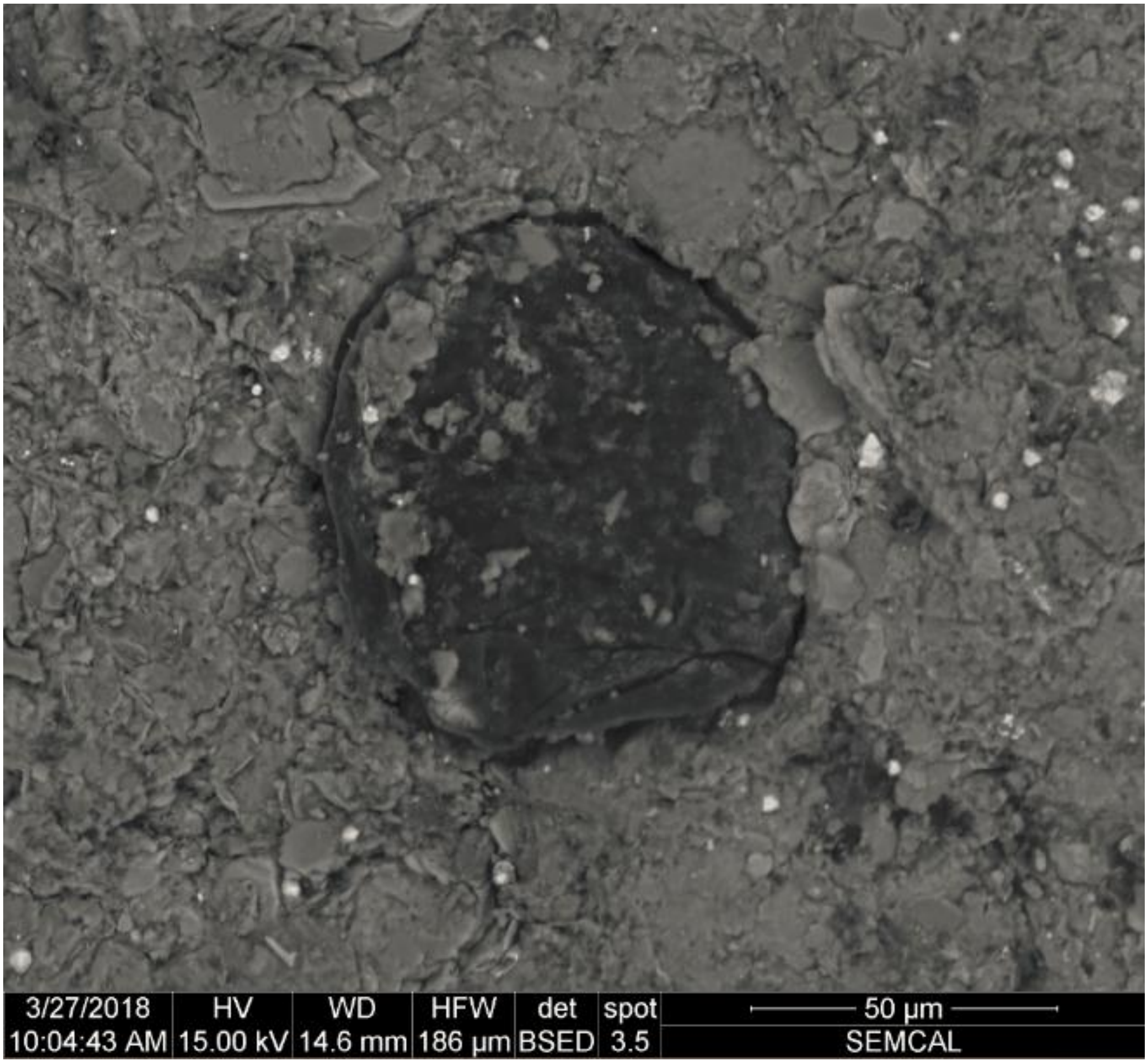

Figure 14. Close-up SEM photomicrograph showing a black spore on the surface of a pyrite concretion.

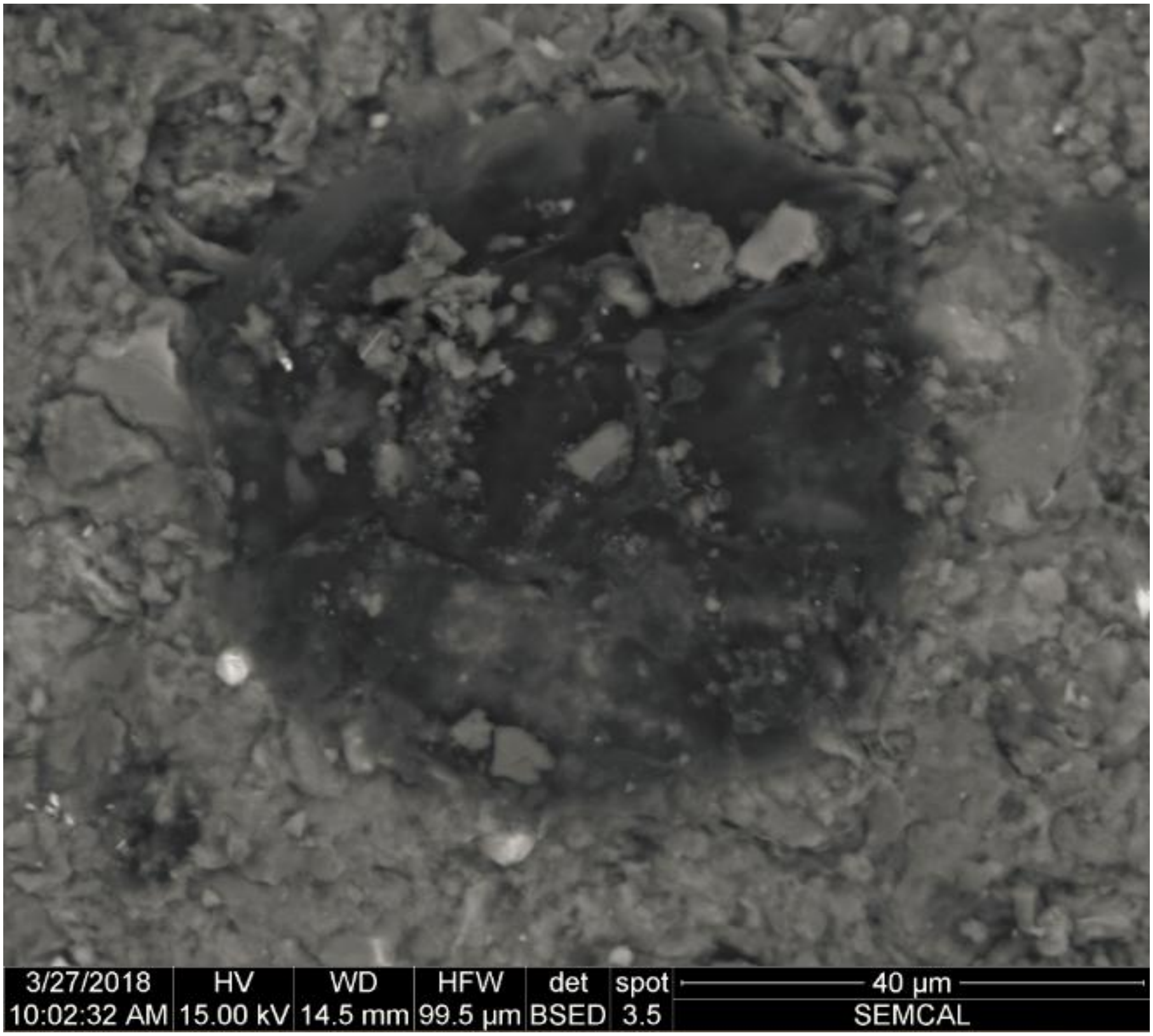

Figure 15. SEM photomicrograph showing a trilete pattern in a *Protosalvinia* spore.

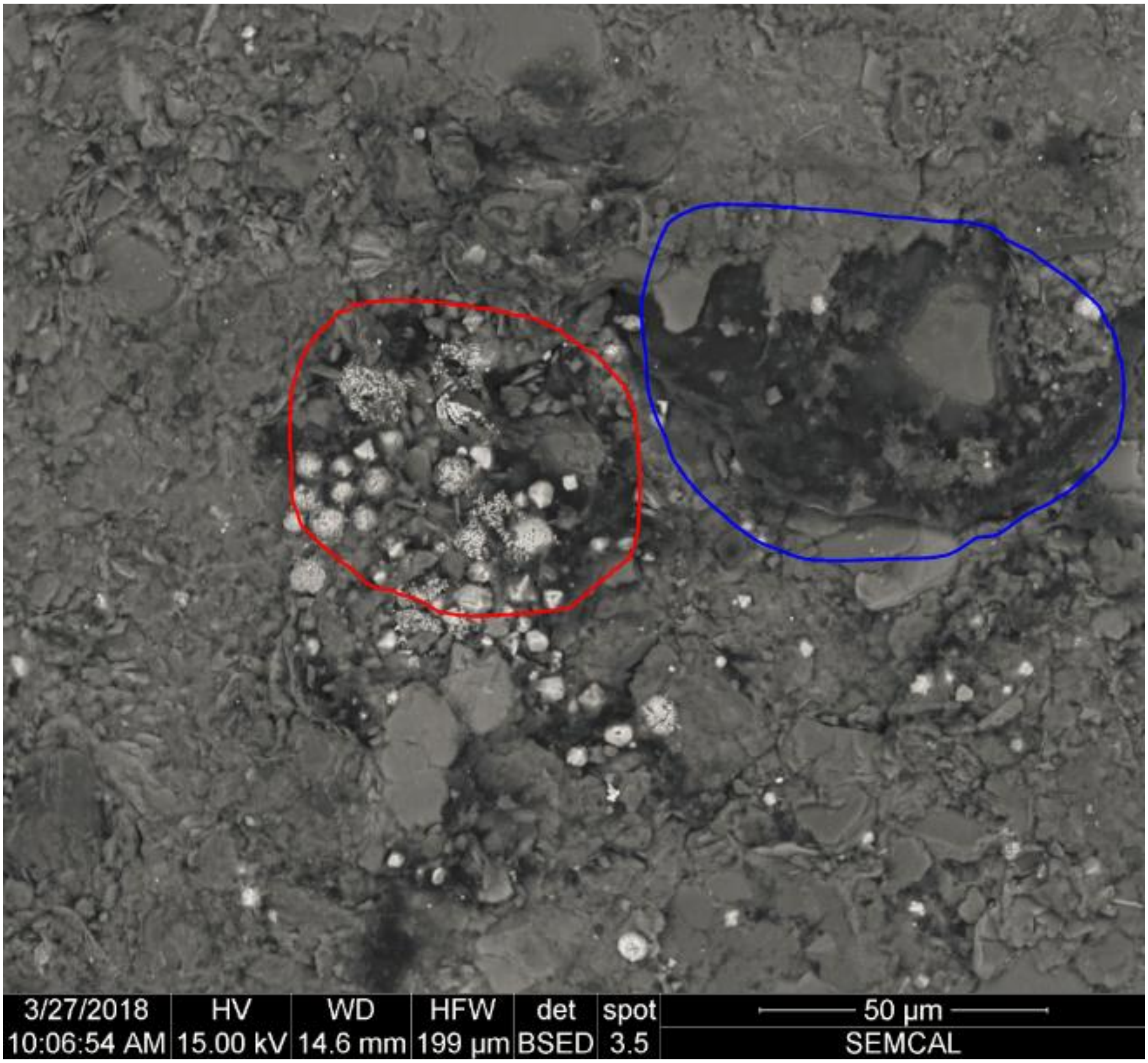

Figure 16. SEM photomicrograph showing one black spore associated with pyrite crystals (red circle) and one black spore not associated with pyrite crystals (blue circle).

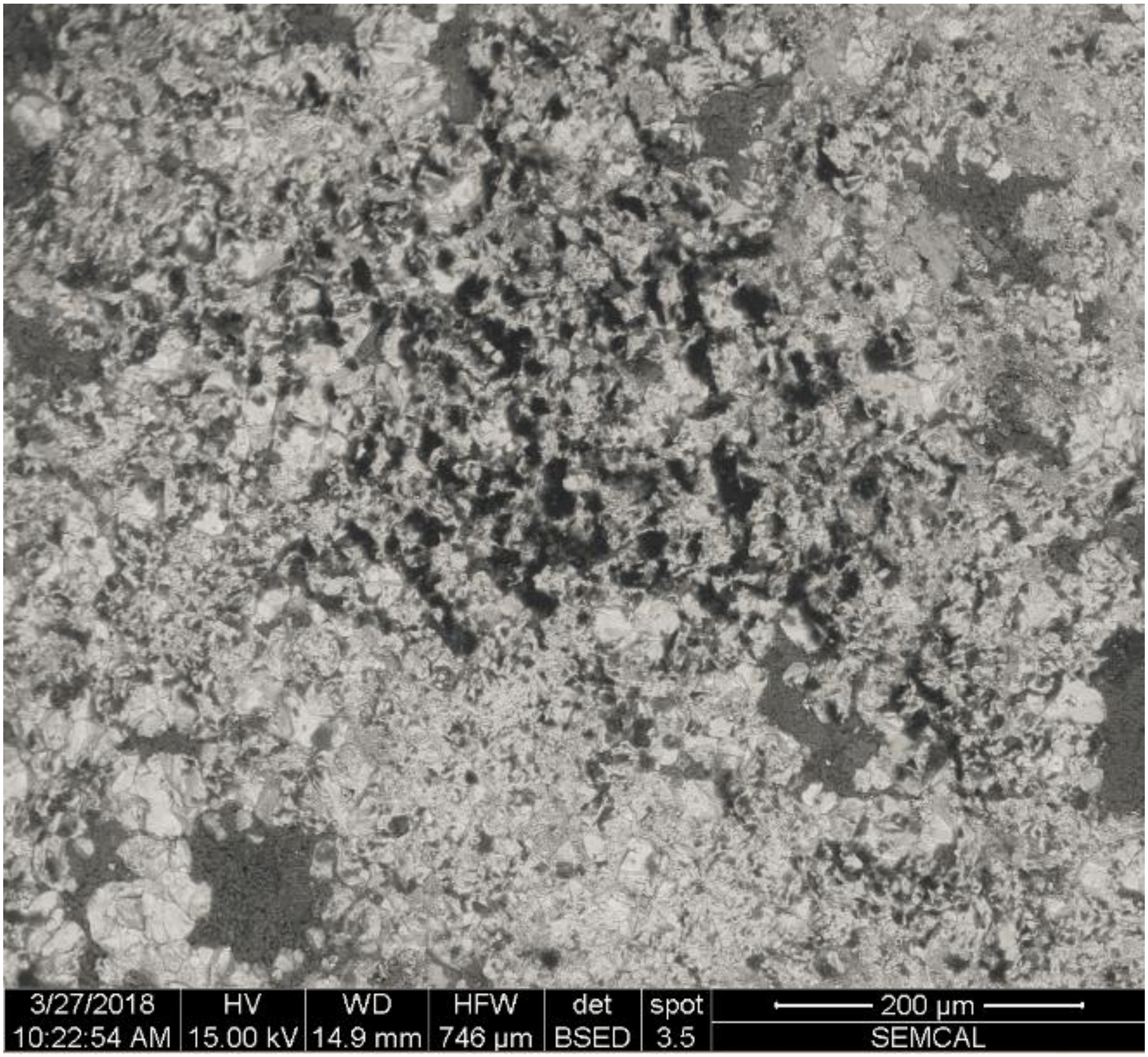

Figure 17. SEM photomicrograph showing organic matter associated with pyrite concretion.

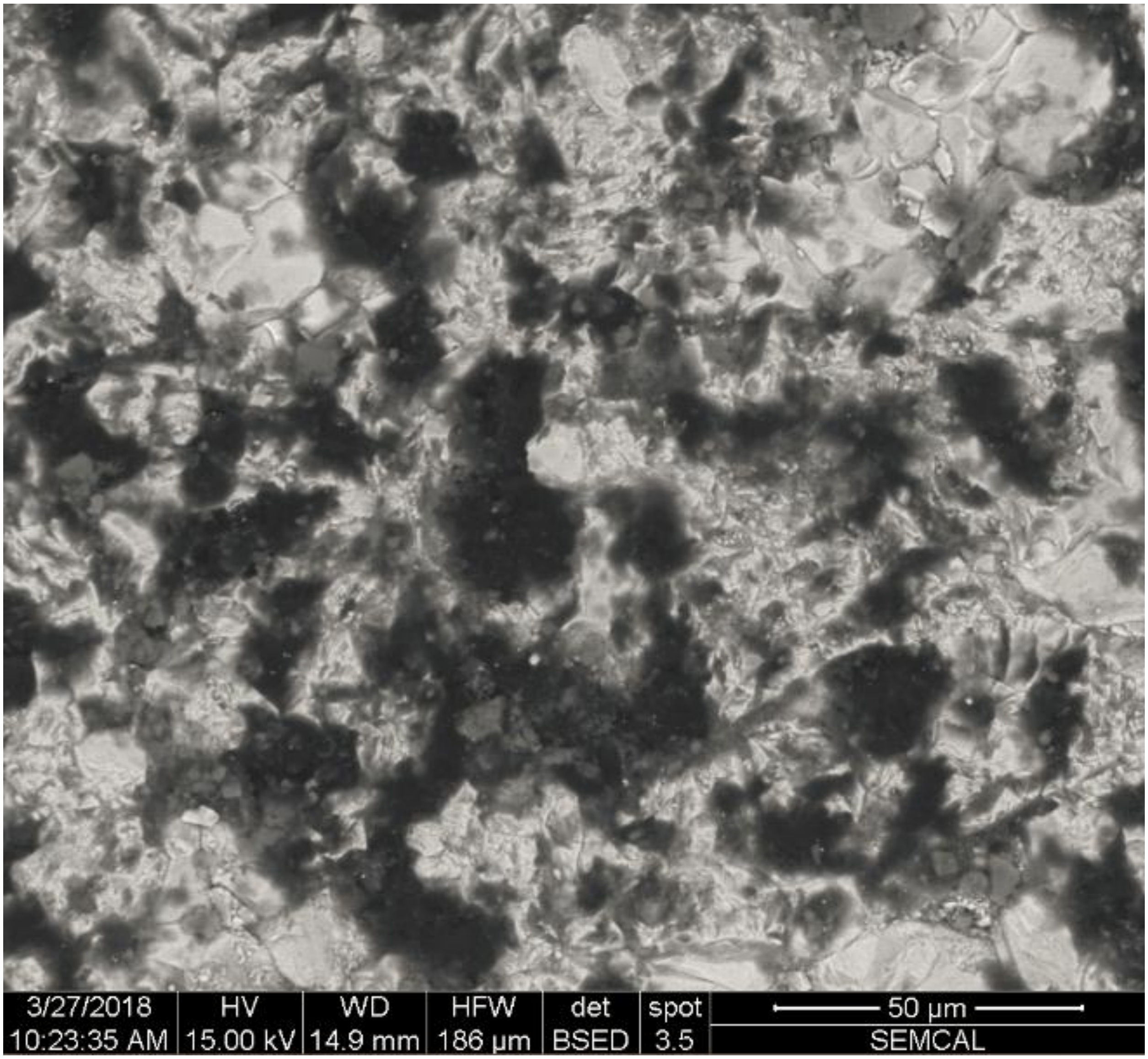

Figure 18. Close-up SEM photomicrograph showing organic matter in a pyrite concretion. Black region is mostly composed of iron and sulfur.

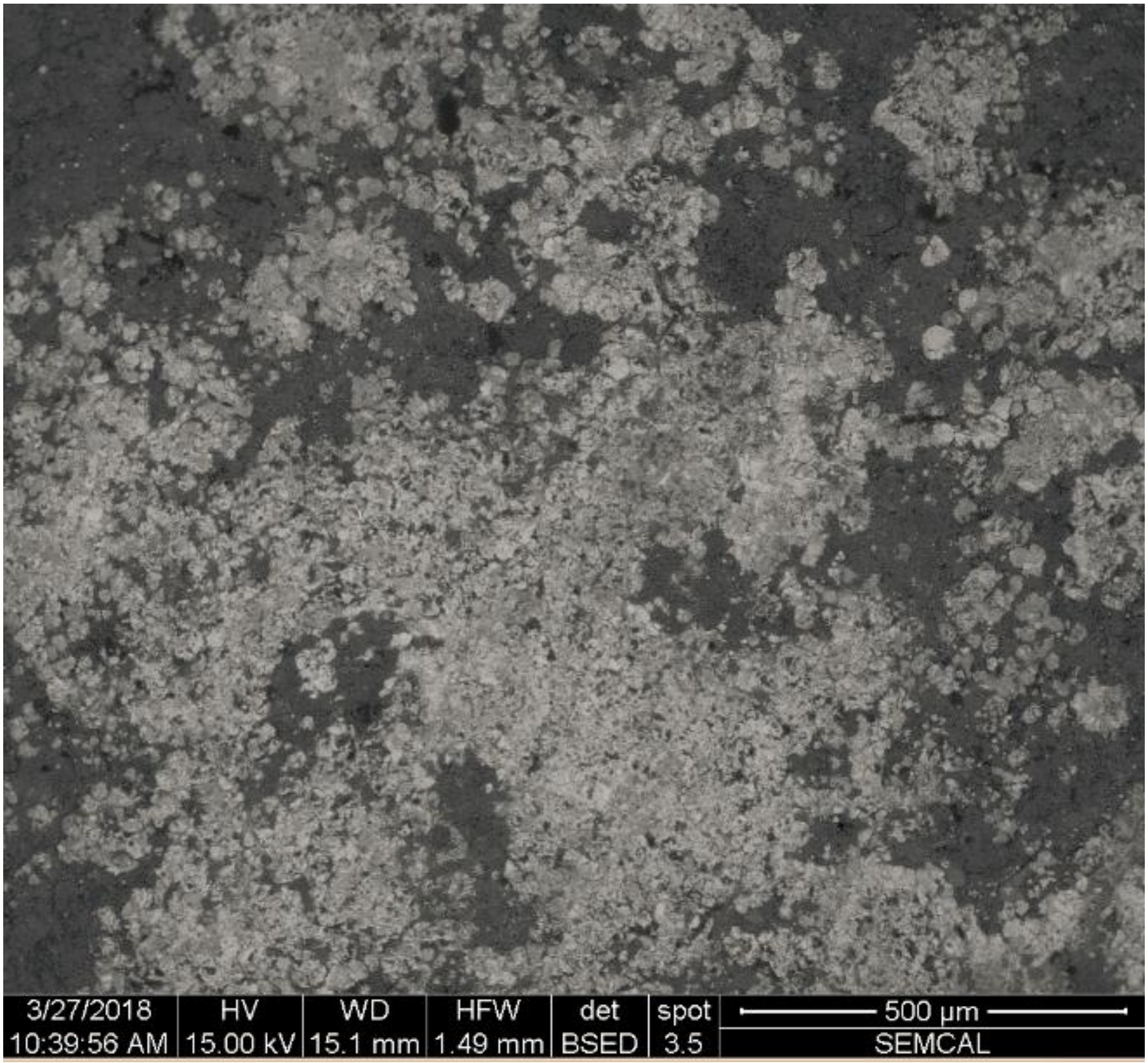

Figure 19. SEM photomicrograph showing the association of organic matter and pyrite on a rock slab.

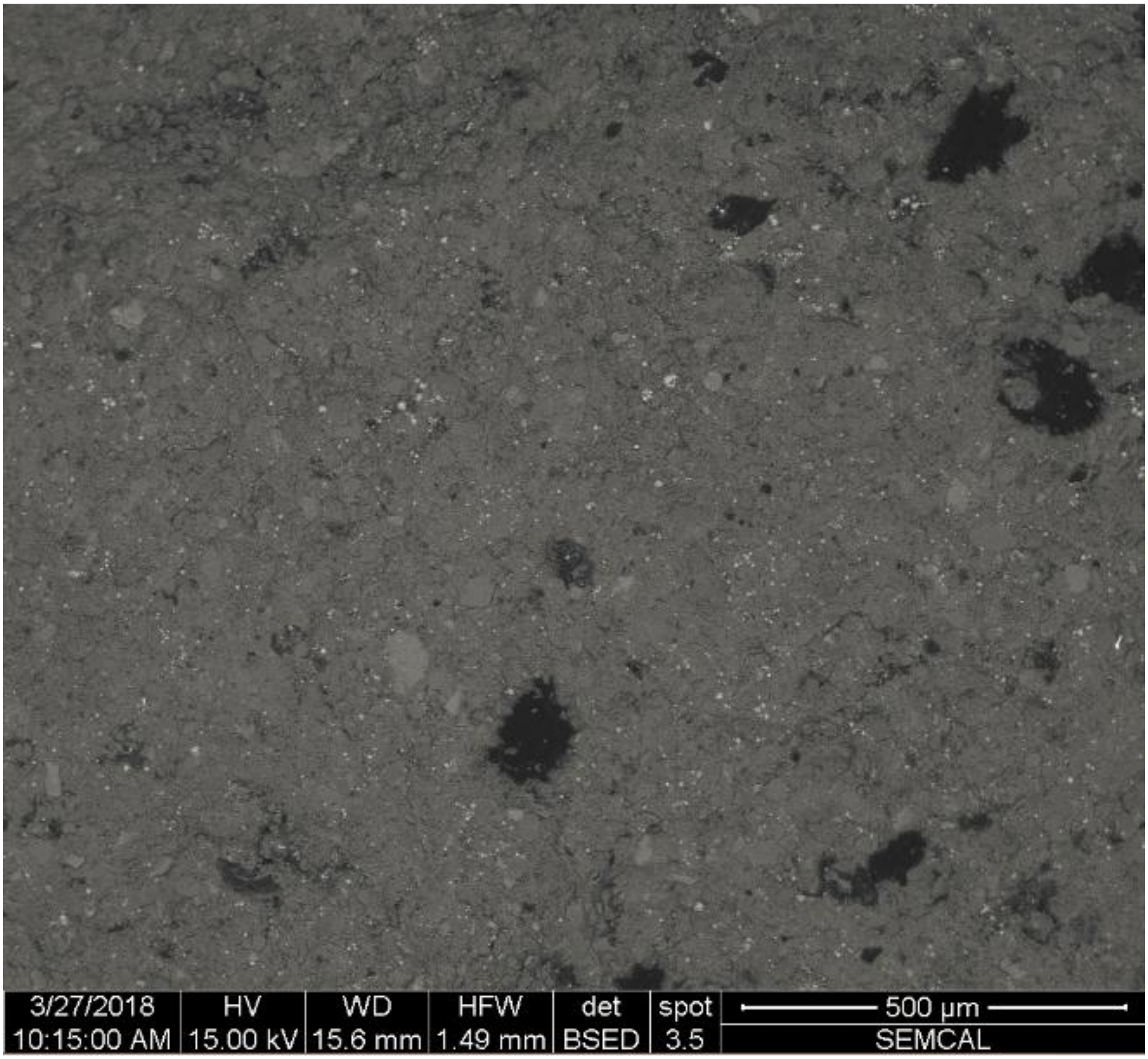

Figure 20. SEM photomicrograph showing large and small spores (in black) on the surface of a pyrite concretion.

Chemical composition from EDX analysis.

From the EDX analysis, the chemical compostion of organic matter includes iron and sulfur. The chemical compostion of the black region in Figure 19 indicates a high carbon value. White regions are typically quartz, silicate and other clay minerals.

Discussion

Biological origin and structure of pyrite concretions.

As shown in the SEM photomicrographs and the macrophotos of studied rock slabs, the origin of the pyrite appears to have been biologically mediated. Large spores are preferentially associated with the pyrite concretions. Biofilm formed because of the rupture of the larger spores and spore capsules. Large spore capsules probably contained the small spores, which were dispersed. Pyrite precipitation was associated with the growth of microbial biofilms.

From what Lester (2017) discovered in pyrite concretions from the Huron Shale Member, the presence of cone-in-cone structures is a crucial morphological feature of the pyrite concretions. Cone-in-cone structures are commonly present in pyrite concretions formed in shale. Cone-in-cone structures are usually associated with organic-rich black shale (Carstens, 1985; Babcock et al. 2015). Moreover, swell structures are a major feature of the small pyrite concretion. Framboids and small euhedral crystals are usually present in the pyrite concretions. I did not observe cone-in-cone structures in any samples that I studied from the Dunkirk Shale Member. However, I did note the presence of a trilete pattern in the studied spore samples from the Dunkirk Shale Member. (Figure 15).

The smaller framboids of pyrite usually were observed to correlate with organic matter. According to the SEM analysis, the framboids ranged in size from 0.2 to 0.6 μm. Each individual euhedral crystal of pyrite represented a bacterial cell and the entire framboid represented a colony (Portillo et al., 2013). Bacteria reduced the H_2S in order to produce pyrite. The sulfur provided by H_2S was produced by the reduction of water sulfates by reducing bacteria that cause pyrite precipitation.

Chemical composition from EDX analysis.

From the EDX analysis, the chemical compostion of organic matter includes iron and sulfur. In Figure 19, the chemical compostion of the black region indicates high carbon values. In the white region are quartz, silicate and other clay minerals within a spores.

Small spores are composed of organic matter, without significant pyrite, and no framboids. Pyrite concretions are formed around large *Protosalvinia* spores, but not around small ones. Pyrite framboids, presumably formed around clusters of bacterial cells, are present in the large spores, and absent from the small spores.

Geological origin and structure of pyrite concretions.

The pyrite horizon in the Dunkirk Shale is laterally correlative with the pyrite horizon in the Huron Shale. However, the two areas are geologically separated by about 460 km. The distribution of the concretions indicates a related origin of each group. This information combined with the earlier conclusion about the origin of pyrite concretion in the Huron Member of the Ohio Shale, supports the interpretation that a large event was responsible for dispersing spores across much of the Appalachian Basin. Spore capsules settling to low-oxygen sediment in the Appalachian Basin probably initiated the formation of pyrite concretions. The only organics associated with the pyrite concretions are microfossils of the genus *Protosalvinia*. Only the larger studied specimen represents spore capsule and the rest of two studied specimens represents spores.

What is *Protosalvinia*? There are two main hypotheses: 1, spores of a terrestrial plant (Niklas and Phillips, 1976; Gray and Boucot, 1979); and 2, spores of a marine brown alga (Schopf, 1978). Although the interpretation of the spores is somewhat ambiguous, Lester (2017) provided information that tends to provide support for a terrestrial plant origin of *Protosalvinia*. Similar information derived here reinforces this hypothesis. Importantly, the taphonomic conditions under which *Protosalvinia* spores are preserved as fossils (as exceptionally preserved organic structures) aligns well with a terrestrial source for the spores that came to rest in a marine depositional setting (see Babcock, 1998).

If *Protosalvinia* represents a land plant, it is possible that the large spores are megaspores, and the small spores are microspores. Alternatively, the large spores may be spore capsules that contained smaller spores (Figure 10).

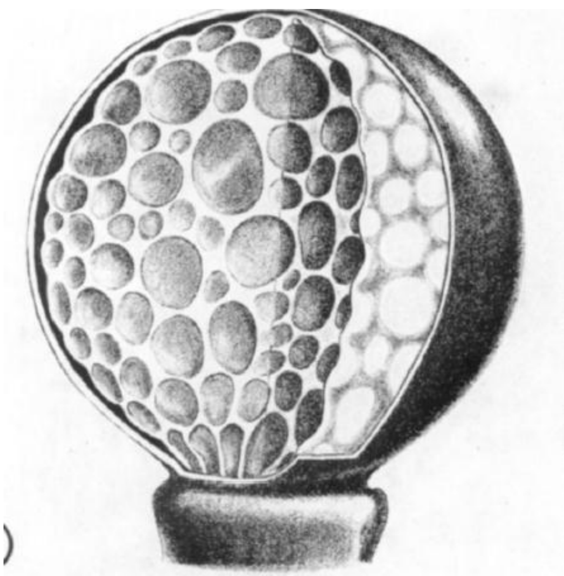

Figure 21. Restoration of multicellular clavate structure of *Protosalvinia* (Niklas and Phillips, 1976)

CONCLUSIONS

The pyrite concretions in the pyrite bed of the Dunkirk Shale Member of the Canadaway Formation at Point Gratiot, New York, apparently formed as organic matter in large *Protosalvinia* spores decayed. *Protosalvinia* spores occur in large and small sizes, and pyrite concretions formed only around the large spores. SEM and EDX analyses show pyrite concretions around large *Protosalvinia* spores but not small ones. Pyrite framboids are associated with the large spores but not the small spores. Pyrite framboids appear to represent pyritization around clusters of bacterial cells.

The origin of pyrite concretions in the Dunkirk Shale Member is similar to that inferred for the origin of pyrite concretions in a pyrite bed in the Huron Shale Member of the Ohio Shale Member of central Ohio (Lester, 2017). The two pyrite horizons are in a similar stratigraphic position, and may be equivalent. It is possible that one large sedimentologic event, or a pair of similar events, dispersed spores widely through the basin during the Late Devonian. The type of event may have been tropical storm or hurricane impinging on the Appalachian Basin coastline.

Suggestions for Future Work

This research project reveals many questions that need further study. First of all, an anoxic environment is typically associated with pyrite concretions. Is there any connection between the formation process of concretions and temperature? This study provides evidence of the biological origin of pyrite. Large euhedral crystals of pyrite protruding from the surface of a pyrite concretion cannot exclude the possibility of some non-biological origins of concretions. In order to more precisely identify a biological origin for pyrite concretions, it is suggested to measure sulfur isotopes ($\delta^{34}S$) in pyrite concretions.

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